21

ON THE POLARISATION OF RAMAN LINES OF SOME ORGANIC COMPOUNDS.

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Plate V

ABSTRACT. The polarisation of the Raman lines of piperidine, ethylene diamine, diethylamine and triethylamine has been experimentally investigated and the symmetry of the first two of these molecules has been discussed. It is shown that the piperidine molecule has a puckered structure having the symmetry C_{1h} and that probably there is no free rotation about the C—C axis in the molecule of ethylene diamine, though there is such a rotation of each of the NH_2 groups about the C—N bonds.

INTRODUCTION.

It is well known that the number of Raman lines which can be observed in the case of any substance depends not only on the number of atoms on the molecule but also on the symmetry possessed by the molecule. It is not possible, however, to determine the symmetry of the molecule from a knowledge of the number of Raman lines alone but besides this, a knowledge of the state of polarisation of the Raman lines also becomes necessary. In the present investigation the polarisation of Raman lines of piperidine, ethylene diamine, diethylamine, and triethylamine has been studied experimentally and an attempt has been made to arrive at a conclusion regarding the structure of the piperidine and ethylene diamine molecules.

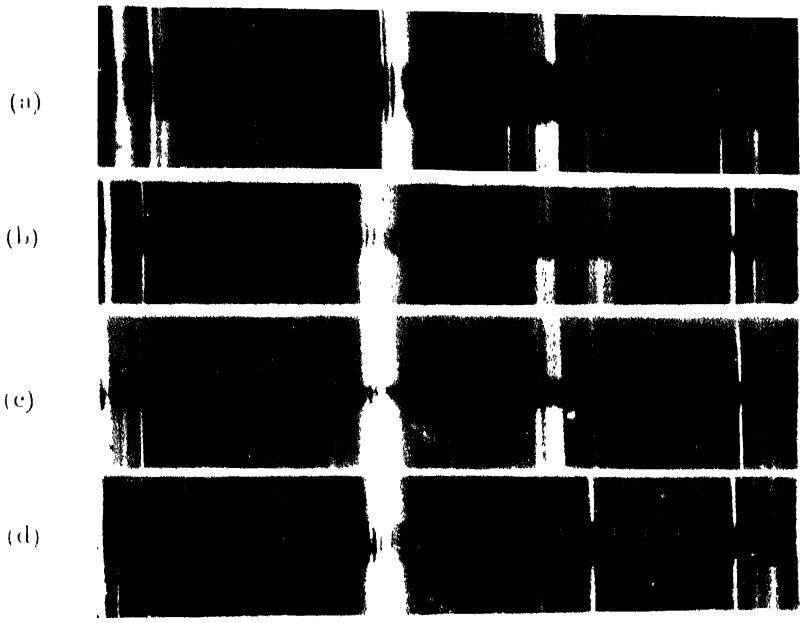
EXPERIMENTAL.

The liquids investigated were all of pure quality and they were distilled in vacuum before being used. The amines were kept in air-tight tubes during exposure because they fumed copiously when brought in contact with atmospheric moisture. The liquids were illuminated by condensing light from a mercury arc on the tubes containing them with the help of a powerful condenser. The double image prism used by Gupta [1] was used in the present investigation in order to photograph the two components of the scattered spectrum simultaneously. As has been mentioned by Gupta, the planes of vibration of the light vector in one of the components is inclined to the vertical at an angle of about 48° when separation of the two components is in the vertical direction. For this reason the axis of the incident beam focussed on the tube was so adjusted by making the axis of the condenser properly inclined to the vertical and placing

the tube and the mercury arc on its axis that the axis of the incident beam was at right angles to the light vector of one of the components of the scattered radiation passing through the double image prism and coincident with the other. Though the adjustment is a little difficult, this peculiar property of the double image prism has one advantage, *viz.*, the two components being inclined to the vertical at an angle very near to 45°, there is appreciably no loss of intensity of any of the components due to reflection at the surfaces of the prisms inside the spectrograph. With the same arrangement the state of polarisation of Raman lines of carbon tetrachloride was studied and it was observed that the observed values reduced to values observed under ideal conditions by Cabannes and Rousset and also by other authors when 0·1 was subtracted from each of these values of ρ, the depolarisation factor. This correction was applied to the results obtained in other cases.

Intensity marks were obtained by the method of variation of width of the slit of the spectrograph used and a standardised tungsten ribbon lamp was used as a source of light for this purpose. The microphotometric records of the spectrograms as well as of intensity marks were obtained with the help of a Moll's microphotometer. Some of the spectrograms contained a little background. In order to correct for this, the total density at the centre of one of the components of any Raman line was first determined and then that of the background was also determined from the microphotometric records. The corresponding intensities were then obtained from the blackening-log intensity curve for the corresponding wave-length and subtracting one from the other, the relative intensity of this component of the Raman line was determined. Similar procedure was adopted to determine the intensity on the same scale of the other component and by dividing the weak component by the strong one, the uncorrected value of ρ was obtained. From this the correction term mentioned above was subtracted and the corrected value of ρ for natural incident light was obtained. The spectrograms have been reproduced in Plate V in order to show how with the arrangement mentioned above, almost the actual state of polarisation is observed on the spectrograms, the loss of the stronger component being very small with this arrangement. It can be seen as for instance, that the line 1442 cm^{-1} due to the deformation oscillation of CH_2 group is almost completely depolarised and when the small correction term is applied, the value reduces to the ideal one, 6/7. The small correction is necessary probably because there was want of transversality of the incident beam.

In some cases where there were overlapping of different Raman lines on one another, a filter of *m*-dinitrobenzene in benzene was used. In the case of piperidine two spectrograms were obtained, one without any filter and the other with a filter of iodine dissolved in carbon tetrachloride. The latter picture showed clearly the state of polarisation of the hydrogen lines having $\Delta\nu$ values greater than 2500 cm^{-1}. The results obtained are tabulated in tables I-IV.



Polarisation of Raman lines

(a) Piperidine

(b) Ethylenediamine

(c) Diethylamine

(d) Triethylamine

TABLE I.

Piperidine $C_6H_{11}N$.

No of Raman lines.	$\Delta\nu$ in cm^{-1} of Raman lines.	Intensity.	Depolarisation factor
1	243	0	dp
2	400	1	p
3	443	1	dp
4	755	0b	7 5
5	817	8	·37
6	857	0	p
7	1006	1	p
8	1085	2	·38
9	1049	2	·89
10	1146	2	·9
11	1265	2	·85
12	1287	2	·54
13	1342	0	dp
14	1442	3b	·88
15	2655	1	p
16	2730	2	·34
17	2803	2	·22
18	2852	4	·25
19	2892	2	·36
20	2931	8b	·34
21	3307	0	p
22	3339	1b	p

TABLE II.

Ethylene diamine $C_2H_8N_2$

No. of Raman lines.	$\Delta\nu$ in cm^{-1} of Raman lines.	I	ρ
1	469	1	·27
2	833	2	·65
3	982	1	·46
4	1100	2	·3
5	1301	1	·82
6	1352	1	·9
7	1443	2	·87
8	2581	4 br	·51
9	2917	2 br	·72
10	3292	8 br	·24
11	3360	4	·68

TABLE III.

Diethylamine $C_4H_{11}N$

No. of Raman lines.	$\Delta\nu$ in cm^{-1} of Raman lines.	I	ρ
1	427	1	·25
2	871	2 br	·32
3	1447	8 br	·9
4	2851	8 br	·44
5	2872	6 br	·63
6	2925	10	·22
7	2970	8	·84
8	3315	4 br	·25

TABLE IV.

Triethylamine $C_6H_{15}N$

No. of Raman lines.	$\Delta\nu$ in cm^{-1} of Raman lines.	I	ρ
1	435	2	·5
2	736	4	·3
3	915	4 br	·9
4	997	1	·68
5	1069	6	·9
6	1286	1	·72
7	1433	8	·86
8	2874	4	·4
9	2932	8 br	·3
10	2966	4	·8

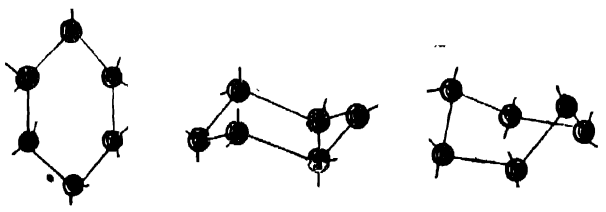
TABLE V.

Carbon tetrachloride CCl_4

No. of Raman lines.	$\Delta\nu$ in cm^{-1} of Raman lines.	I	ρ
1	217	8	·86
2	313	8	·78
3	459	10	·05
4	763	6	·86
5	792	6	·86

DISCUSION OF RESULTS.

Piperidine—The symmetry of the piperidine molecule has been discussed recently by Kohlrausch and Stockmair [2] but no definite conclusion could be drawn by them regarding the symmetry of the molecule because the data for polarisation of the Raman lines were not available. The molecule may have either a plane or puckered structure. In the case of the plane structure the symmetry would be C_{2v}, the twofold axis of rotation passing through the nitrogen atom and the diametrically opposite carbon atom and one of the two planes of reflection passing through this axis lies in the plane of the molecule, the other being perpendicular to the plane as shown in figure 1 (*a*). In the case of the puckered structure, it may have again two forms, both having the same symmetry C_{1h}, one being called "Sessel" and the other "Wannen" form as shown in figures 1 (*b*) and 1 (*c*) respectively. The latter two forms cannot be distinguished from each other from a study of the polarisation of the Raman lines but it can be decided whether the molecule has a plane structure or a puckered one.



(*a*) (*b*) (*c*)

FIGURE 1.

As there are altogether 17 atoms in the piperidine molecule, the maximum number of lines in the Raman spectrum may be $51-6=45$ in the case of the plane as well as the puckered structure. The forms of vibration of the ring as well as of the CH_2 group of the cyclohexane molecule have been shown diagramatically by Kohlrausch and Stockmair in the paper mentioned above. These forms of vibration of the closed ring of the piperidine molecule as well as those of the CH_2 group are reproduced in figure 2. In a more recent paper Kahovec and Kohlrausch [3] have deduced the number of possible polarised and depolarised lines which would

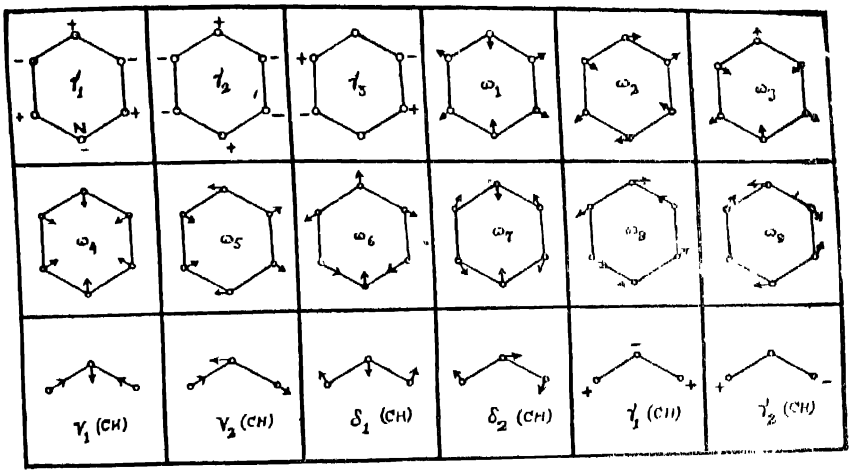


FIGURE 2.

be expected in the case of the piperidine molecule if it would have the symmetry C_{1h} ($=C_s$), *i.e.*, if the molecule would have a puckered structure. These lines are listed in table V, the lines due to N – H group not being included in the table. The letters "s" and "as" denote symmetric and anti-symmetric to the plane; similarly "p" and "dp" denote respectively polarised and depolarised.

TABLE V.

σ_y		Piperidine – C_{1h}	
s	p	γ_1 γ_2 ω_1 ω_3 ω_4 ω_6 ω_7	$3\gamma_1$ $2\gamma_2$ $3\delta_1$ $2\delta_2$ $3\nu_1$ $2\nu_2$
as	d p	γ_2 ω_2 ω_5 ω_8 ω_9	$2\gamma_1$ $3\gamma_2$ $2\delta_1$ $3\delta_2$ $2\nu_1$ $3\nu_3$
		Vibrations of the ring	CH vibrations

The different CH vibrations arise from the different phase relations among these vibrations of the individual CH_2 groups present in the whole molecule. As for instance, the movement of the carbon atom in the case of δ_1 and ν_1 oscillations of the CH_2 groups is of identical nature and also only those vibrations of the ring in which similar movements of the carbon atoms take place can give rise to δ_1 and ν_1 (CH) oscillations; hence there are as many δ_1 (CH) oscillations as there are ν_1 (CH) oscillations. Similarly there are as many δ_2 (CH) oscillations as there are ν_2 (CH) oscillations. It can be seen from table V that there should be 5 polarised Raman lines ($3\ \nu_1$ and $2\ \nu_2$) having $\triangle\ \nu$ greater than 2500 cm^{-1} if the symmetry of the molecule be C_{1h}. If, however, the molecule would have a planar structure, the symmetry would be C_{2v} and the two (CH) vibrations $2\ \nu_2$ which are symmetric to the plane of symmetry would be antisymmetric to the twofold axis of rotation passing through the nitrogen atom and the carbon atom opposite to it, and in that case these lines would be depolarised. Hence for the planar structure there can be only 3 (CH) oscillations of frequencies greater than 2500 cm^{-1} which are polarised. Actually, however, there are six such polarised lines, as can be seen from table I. It can therefore be definitely concluded that the structure of the piperidine molecule is a puckered one. Probably one of these six lines is not due to any fundamental oscillation.

In an attempt to identify the frequencies of oscillations of the ring, Kahovec and Kohlrausch have pointed out that in the case of piperidine; $\omega_4 = 807$ cm^{-1}, This line is intense and is observed to be well polarised by the present author, and therefore the above assignment seems to be quite correct. The authors mentioned above have not arrived at any definite conclusion regarding the other frequencies. An attempt may be made here to identify the other frequencies also, after the state of polarisation of the lines is known. In the case of the cyclohexane molecule, each of the pairs of oscillations, $\omega_{1,2}$, $\omega_{5,6}$ and $\omega_{7,8}$ gives a twofold degenerate line which is depolarised. When one of the carbon atoms is replaced by a nitrogen atom as in the piperidine molecule, the degeneracy is removed and three pairs of lines are expected to be produced by these six modes of vibration. As can be seen from figure 2, of these vibrations ω_1, ω_6 and ω_7 ought to give polarised Raman lines and ω_2, ω_5 and ω_8 depolarised Raman lines. As has been pointed out by Kahovec and Kohlrausch, $\omega_{1,2}$ in the case of cyclohexane can be identified with the line 425 cm^{-1}, though the actual calculation, taking ω_1 equal to 809 cm^{-1} gives $\omega_{1,2} = 520$ cm^{-1}. In the case of piperidine the lines in this region are 400 cm^{-1} and 443 cm^{-1}; the former being polarised and the latter depolarised, they can respectively represent ω_1 and ω_2. Similar arguments lead to the conclusion that probably the lines 1035 cm^{-1}, 1049 cm^{-1}, 1265 cm^{-1} and 1287 cm^{-1} represent ω_6, ω_5, ω_8 and ω_7 respectively. Kahovec and Kohlrausch have suggested that ω_3 lies in the region 755 cm^{-1}. This line, however, does not seem to be well polarised; on the other hand, the line 857 (0) is well polarised and may be identified with ω_3.

The existence of the line 1006 cm^{-1} in the case of piperidine is confirmed by the present investigation. There is also a polarised line at 3307 cm^{-1} which is feeble and was observed by Sirkar[4] previously but the presence of this line is not expected from theoretical point of view. Probably, piperidine being highly hygroscopic, a small percentage of molecules being acted upon by moisture gives rise to this line.

Ethylene diamine.

It can be seen from table II that of the two lines 3292 cm^{-1} and 3360 cm^{-1} due to the N-H vibration of the NH_2 group the former is well polarised and the latter completely depolarised. Since there are two NH_2 groups in the molecule a knowlege of their relative orientations in the molecule is necessary in order to ascertain which types of vibrations are responsible for these two lines. The structure of the molecule has been discussed by Zahn[5] who has concluded from the results of measurement of the permanent electric moment of the molecule that the observed value of μ agrees with the value calculated with the assumption that either (1) there is free rotation about the two C–C bonds and about C–N bonds, or (2) there is free rotation of the two NH_2 groups in the transposition about the C–C bonds. It can be easily seen that if the two NH_2 groups were fixed in the trans position the molecule would possess a centre of symmetry and a plane of reflection and the symmetric vibration of the two NH_2 groups in phase ν_1, (π, s) would be intense and well polarised in the Raman effect but in that case the value of ρ would be zero. Hence the free rotation of the NH_2 groups has to be taken into consideration. In the case (2) of such a free rotation of the NH_2 groups about the C–N bond, the centre of symmetry as well as the plane of reflection are absent for most of the time in one complete rotation and therefore the two groups vibrate independent of each other, there being absolutely no phase relation between the vibrations of the two NH_2 groups, so that the polarisation character of these Raman lines depend on the character of the oscillations of the single group and thus the symmetric vibration gives the line 3292 cm^{-1} and the completely depolarised line 3360 cm^{-1} ($\rho=\frac{6}{7}$) is due to antisymmetric vibration of each group. At the time of such vibration, the CN bond also undergoes a little deformation but that does not affect very much the frequency of the vibration of the NH_2 groups, because even in the case of the ethylene molecule the vibration ν_1 (π, s) which entails an expansion and contraction of the C=C bond, the frequency is 3719 cm^{-1}, *i.e.*, only slightly higher than the normal value of the vibration of the comparatively free CH_2 group. Kohlrausch[6] has calculated the angle α between NH bonds and in the NH_2 group by assuming the mean value of ν (π) ν (σ) and δ (π) to be 3313 cm^{-1}, 3367 cm^{-1} and 1113 cm^{-1} respectively. In the present case an attempt may be made

to find the value of f and α by assuming a valence force system and with

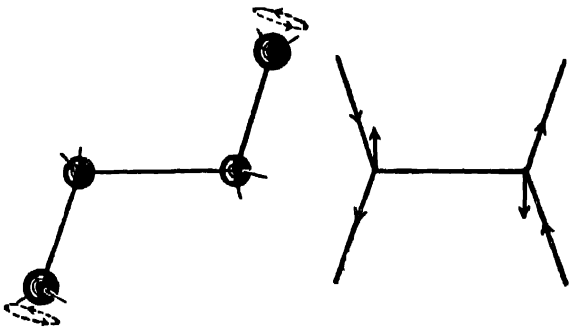


FIGURE 3. FIGURE 4.

the help of the simplified formulae,

$$\nu(\pi) = \frac{f}{m}\left[1-(1-p)\cos^2\frac{\alpha}{2}\right]$$

and $$\nu(\sigma) = \frac{f}{m}\left[p+(1-p)\cos^2\frac{\alpha}{2}\right],$$

the values of f and α are found to be $6{\cdot}053\times10^5$ dynes/cm. and 107° 48′ respectively. As regards the polarisation characters of the two lines 2851 cm^{-1} and 2917 cm^{-1}, it can be definitely stated that both of these two lines are partially polarised and none of them is completely depolarised. If it is assumed that the two CH_2 groups are so arranged in the molecule that there is a centre of symmetry when only these two groups are taken into consideration, as shown in figure 3 the vibration antisymmetric to the centre of symmetry will be forbidden and only those symmetric to the centre of symmetry will be observed in Raman effect. The symmetric C−H valence oscillation of the two groups in phase with each other will be most intense and polarised and probably the line 2851 cm^{-1} can be identified with this vibration ; the other line 2917 cm^{-1} is probably due to the vibration shown in figure 4 in which the centre of symmetry is retained. If this view be correct, it can be concluded that there is no free rotation round the C−C axis in this particular molecule. Since there is no doubt regarding the free rotation of the NH_2 group and as due to such a rotation the antisymmetric vibration of the NH_2 group is completely depolarised, it might be expected that if the rotation about C−C axis were present, one of the Raman lines due to C−H valence oscillation would be completely depolarised. Since actually it is not so, the above conclusion, that probably there is no rotation about the C−C

axis is drawn. The angle between two C−H bonds in a CH_2 group calculated by applying the valence force system is about 105° 36′ which shows that actually the angle may be about the tetrahedral angle.

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